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FOR: LITHIUM-COBALT COMPOSITE OXIDE, PROCESS FOR ITS
PRODUCTION, POSITIVE ELECTRODE FOR LITHIUM
SECONDARY CELL EMPLOYING IT, AND LITHIUM SECONDARY
CELL

DECLARATION

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I hereby declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

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January 15, 2007
Date

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【TYPE OF DOCUMENT】 SPECIFICATION

【TITLE OF THE INVENTION】

LITHIUM-COBALT COMPOSITE OXIDE AND PROCESS FOR ITS
PRODUCTION

5 【SCOPE OF THE CLAIM(S)】

【Claim 1】

A hexagonal lithium-cobalt composite oxide for a lithium secondary cell, which is represented by the formula $\text{LiCo}_{1-x}\text{M}_x\text{O}_2$, wherein x is $0.0005 \leq x \leq 0.02$ and M is at least one member selected from the group consisting of Zr and Hf, and which has a half-width of the diffraction peak for (110) face at $2\theta = 66.5 \pm 1^\circ$, of from 0.080 to 0.180° , as measured by the X-ray diffraction using CuK_α as a ray source.

15 【Claim 2】

The hexagonal lithium-cobalt composite oxide for a lithium secondary cell according to Claim 1, wherein x is $0.001 \leq x \leq 0.01$, and the half-width of the diffraction peak for (110) face is from 0.100 to 0.165° .

20 【Claim 3】

A process for producing the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in Claim 1 or 2, which comprises dry blending a cobalt oxyhydroxide powder having an average particle size of from 1 to $20 \mu\text{m}$ and a specific surface area of from 2 to $200 \text{ m}^2/\text{g}$, a lithium carbonate powder having an average

particle size of from 1 to 50 μm and a specific surface area of from 0.1 to 10 m^2/g , and a powder of an oxide of metal element M having an average particle size of at most 10 μm and a specific surface area of from 1 to 100 m^2/g , and firing the mixture at a temperature of from 850 to 1,000°C for from 4 to 30 hours in an oxygen-containing atmosphere.

【DETAILED DESCRIPTION OF THE INVENTION】

【Technical Field to which the Invention Belongs】

10 The present invention relates to an improved lithium-cobalt composite oxide for a lithium secondary cell, and a process for its production.

【Prior Art】

15 In recent years, along with the progress in portable or codeless equipments, a demand is mounting for a non-aqueous electrolyte secondary cell which is small in size and light in weight and has a high energy density. As an active material for a non-aqueous electrolyte secondary cell, a composite oxide of lithium and a transition
20 metal, such as LiCoO_2 , LiNiO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, LiMn_2O_4 or LiMnO_2 , has been known.

25 Especially, a lithium secondary cell employing a lithium-cobalt composite oxide (LiCoO_2) as a positive electrode active material and employing a lithium alloy or a carbon such as graphite or carbon fiber as a negative electrode, provides a high voltage at a level of 4 V and is widely used as a cell having a high energy

density.

However, a non-aqueous secondary cell has had a problem of deterioration of the cycle characteristics such that the cell discharge capacity gradually decreases
5 as a charge/discharge cycle is repeated, or a problem that the reduction of discharge capacity is large at a low temperature.

In order to improve such cell properties, JP-A-7-32017 proposes to replace from 5 to 35% of Co atoms with
10 W, Mn, Ta, Ti or Nb, for improvement of the cycle characteristics of a lithium secondary cell. Further, JP-A-6-64928 proposes to improve the self-discharge characteristics of a lithium secondary cell by using a Ti-containing lithium-cobalt composite oxide prepared by
15 a synthesis employing a molten salt.

Further, JP-A-10-1316 proposes a production method of dispersing in an aqueous lithium hydroxide solution e.g. cobalt hydroxide or cobalt oxyhydroxide wherein the valence of cobalt is trivalent, followed by heat
20 treatment, for the purpose of improving the cycle characteristics, etc. Further, JP-A-10-279315 proposes to obtain an active material having a high capacity and good cycle characteristics by firing e.g. dicobalt trioxide (Co_2O_3) or cobalt oxyhydroxide wherein the
25 valence of cobalt is trivalent, with e.g. lithium oxide at a temperature of from 250 to 1,000°C.

Further, JP-A-10-312805 proposes to improve the

cycle characteristics by using as a positive electrode active material LiCoO_2 of a hexagonal system having a crystallite diameter of from 45 to 100 nm in a (110) direction of the crystallite, wherein the length of c axis of lattice constant is at most 14.051 Å.

【Problems that the Invention is to Solve】

However, with respect to a lithium secondary cell using LiCoO_2 as a positive electrode active material, no product has been known which fully satisfies all of requirements for cycle characteristics, the initial weight capacity density and the low temperature operation efficiency, and for a production method for efficient mass production.

It is an object of the present invention to provide a positive electrode active material for a lithium secondary cell which has a large electric capacity and good discharge characteristics at low temperatures, is excellent in the charge/discharge cycle durability, and has high safety, and a process for its production.

【Means of Solving the Problems】

The present inventors have found that when an active material having a specific composition and crystal structure, is excellent in the cell properties, and particularly, an active material obtained by a specific production process is especially excellent in cycle characteristics, low temperature operation efficiency and productivity.

The present invention provides a hexagonal lithium-cobalt composite oxide for a lithium secondary cell, which is represented by the formula $\text{LiCo}_{1-x}\text{M}_x\text{O}_2$, wherein x is $0.0005 \leq x \leq 0.02$ and M is at least one member selected from the group consisting of Zr and Hf, and which has a half-width of the diffraction peak for (110) face at $2\theta = 66.5 \pm 1^\circ$, of from 0.080 to 0.180° , as measured by the X-ray diffraction using CuK_α as a ray source.

If x is smaller than 0.0005 , the cycle durability and low temperature operation efficiency improvement effect decrease, such being undesirable. If x is larger than 0.02 , the initial electric capacity decreases, such being undesirable. In the present invention, x is preferably $0.001 \leq x \leq 0.01$, particularly preferably $0.002 \leq x \leq 0.007$.

The half-width of the diffraction peak for (110) face at $2\theta = 66.5 \pm 1^\circ$, as measured by the X-ray diffraction using CuK_α as a ray source, reflects the crystallite diameter in a certain specific direction of the lithium-containing composite oxide, and a relation has been found such that the larger the half width, the smaller the crystallite diameter. In the present invention, the half-width of the peak means the width of the peak at $1/2$ of the height of the peak.

The half-width of the diffraction peak for (110) face of the present invention is from 0.080 to 0.180° . If such a half-width is less than 0.080° , the

charge/discharge cycle durability, initial electric capacity, average discharge voltage or safety of the cell employing it as a positive electrode active material, tends to deteriorate, such being undesirable. If such a
5 half-width exceeds 0.180° , the initial electric capacity and safety of the cell tend to be low, such being undesirable. A particularly preferred range is from 0.100 to 0.165° .

Further, the present invention provides a process
10 for producing a hexagonal lithium-cobalt composite oxide for a lithium secondary cell, which comprises dry blending a cobalt oxyhydroxide powder having an average particle size of from 1 to $20\text{ }\mu\text{m}$ and a specific surface area of from 2 to $200\text{ m}^2/\text{g}$, a lithium carbonate powder
15 having an average particle size of from 1 to $50\text{ }\mu\text{m}$ and a specific surface area of from 0.1 to $10\text{ m}^2/\text{g}$, and a powder of an oxide of metal element M having an average particle size of at most $10\text{ }\mu\text{m}$ and a specific surface area of from 1 to $100\text{ m}^2/\text{g}$, followed by firing from 850
20 to $1,000^\circ\text{C}$ from 4 to 30 hours in an oxygen-containing atmosphere.

In the present invention, the average particle size means a weight average particle diameter. In the present invention, the weight average particle diameter is a
25 particle size at a point where the cumulative curve of mass becomes 50% in the cumulative curve for the total mass of 100% prepared by obtaining the particle size

distribution based on mass. This may be referred to also as a mass base cumulative 50% diameter (for example, Chemical Engineering Handbook "Fifth Edition" (compiled by Chemical Engineering Association) p 220-221. The measurement of the particle size is carried out by thoroughly dispersing in a medium such as water by means of e.g. ultrasonic treatment and measuring the particle size distribution (for example, by using Microtruck HRAX-100, manufactured by Nikkiso co., Ltd.).

10 In the present invention, cobalt oxyhydroxide having specific properties is used as a cobalt material. If the average particle size of the cobalt oxyhydroxide is less than 1 μm , the safety of the cell tends to decrease, or the packing density of the positive electrode layer tends to decrease, whereby the electrical capacity per volume tends to decrease, such being undesirable. Further, if the average particle size of the cobalt oxyhydroxide exceeds 20 μm , the discharge characteristics of the cell at a large current tend to decrease, such being undesirable. A preferred average particle size of the cobalt oxyhydroxide is from 4 to 15 μm . The cobalt oxyhydroxide may sometimes be produced in a hydrous state. In such a case, the specific surface area can hardly be measured. Accordingly, in the present invention, the specific surface area of hydrous cobalt oxyhydroxide means the specific surface area with respect to a powder obtained by drying the hydrate at 120°C for

16 hours for dehydration.

In the present invention, when hydrous cobalt oxyhydroxide is to be used, it is preferred to use a powder after drying it. For example, it is preferred to employ it after drying at 120°C for 16 hours. In the present invention, if the specific surface area of the cobalt oxyhydroxide is less than 2 m²/g, the discharge capacity at a large current tends to decrease, such being undesirable. Further, if the specific surface area of the cobalt oxyhydroxide exceeds 200 m²/g, the packing density of the positive electrode layer tends to decrease, whereby the electric capacity per volume tends to decrease, such being undesirable. A preferred specific surface area of the cobalt oxyhydroxide is from 20 to 100 m²/g.

For the process of the present invention, it is preferred to use lithium carbonate having a specific nature, as a lithium material. If the average particle size of the lithium carbonate is less than 1 μm, the bulk density of the powder tends to decrease, and the productivity in mass production tends to decrease, such being undesirable. Further, if the average particle size of the lithium carbonate exceeds 50 μm, the initial electric capacity tends to decrease, such being undesirable. A particularly preferred average particle size of the lithium carbonate is from 5 to 30 μm. If the specific surface area of the lithium carbonate is less

than $0.1 \text{ m}^2/\text{g}$, the initial discharge capacity per unit weight tends to decrease, such being undesirable.

Further, if the specific surface area of the lithium carbonate exceeds $10 \text{ m}^2/\text{g}$, the packing density of the

5 positive electrode layer tends to decrease, whereby the electric capacity per volume tends to decrease, such being undesirable. A particularly preferred specific surface area of the lithium carbonate is from 0.3 to $3 \text{ m}^2/\text{g}$.

10 In the present invention, a metal oxide having a specific nature is used as a metal oxide raw material containing element M. As the metal oxide containing element M, when M is zirconium (Zr), ZrO_2 may be mentioned, and when M is hafnium (Hf), HfO_2 may be
15 mentioned.

If the average particle size of the metal oxide exceeds $10 \text{ }\mu\text{m}$, the distribution of element M in the positive electrode active material particles tends to be non-uniform, whereby the effects of adding element M
20 relating to the cell performance tend to decrease, such being undesirable. A preferred average particle size of the oxide of metal element M is at most $1 \text{ }\mu\text{m}$, particularly preferably at most $0.3 \text{ }\mu\text{m}$.

If the specific surface area of the oxide containing
25 metal element M is less than $1 \text{ m}^2/\text{g}$, the reactivity tends to decrease, whereby the effects of adding element M relating to the cell performance tend to decrease, such

being undesirable. On the other hand, if the specific surface area of the metal oxide containing element M exceeds 100 m²/g., element M tends to be uniformly incorporated into the crystal lattice, whereby the effects of adding metal element M relating to the cell performance tend to decrease, such being undesirable. A preferred specific surface area of the oxide of metal element M is from 2 to 20 m²/g.

The lithium-cobalt composite oxide of the present invention is obtained by dry blending the cobalt oxyhydroxide powder, the lithium carbonate powder and the oxide powder containing element M, followed by firing from 850 to 1,000°C for from 4 to 30 hours in an oxygen-containing atmosphere. Wet blending is not preferred, since the productivity is low. If the firing temperature is lower than 850°C, the charge/discharge cycle durability tends to be low, such being undesirable. On the other hand, if the firing temperature exceeds 1,000°C, the initial electric capacity tends to decrease, such being undesirable. Particularly preferred is from 880 to 920°C. If the firing time is less than 4 hours, the firing state tends to be non-uniform during mass production, whereby fluctuation is likely to result in the properties, such being undesirable. If it exceeds 30 hours, the productivity tends to decrease, such being undesirable. It is particularly preferred to employ a firing time of from 8 to 20 hours.

It is necessary to carry out the firing in an oxygen stream. The oxygen concentration in the stream is preferably from 10 to 100 volume%, particularly preferably from 19 to 50 volume%. If the oxygen concentration is low, the cell performance of the active material tends to deteriorate, such being undesirable.

The positive electrode active material obtained by the process of the present invention and having the specific value of the half-width of the diffraction peak for (110) face, has a higher low temperature operation efficiency than ever, and is excellent in the charge/discharge cycle durability, while maintaining the initial electric capacity.

A positive electrode composite material is obtained by blending the composite oxide powder of the present invention with a binder and a carbon type conductive material such as acetylene black, graphite or ketjenblack. As the binder, polyvinylidene fluoride, polytetrafluoroethylene, polyamide, carboxymethyl cellulose or an acrylic resin may, for example, be employed.

A dispersion made of a kneaded product or a slurry comprising the powder of the composite oxide of the present invention, an electrically conductive material, a binder and a solvent or dispersant for the binder, is coated on a positive electrode current collector made of e.g. an aluminum foil or a stainless steel foil, and then

have it supported on the current collector to obtain a positive electrode plate. As the separator, a porous polyethylene film or a porous polypropylene film may, for example, be employed.

5 In the lithium cell using the positive electrode active material of the present invention, as the solvent for the electrolyte solution, a carbonic ester is preferred. The carbonic ester may be cyclic or chain. The cyclic carbonic ester may, for example, be propylene
10 carbonate or ethylene carbonate (EC). The chain carbonic ester may, for example, be dimethyl carbonate, diethyl carbonate (DEC), ethylmethyl carbonate, methylpropyl carbonate or methylisopropyl carbonate.

 In the present invention, the above carbonic esters
15 may be used alone or in combination as a mixture of two or more of them. Further, such an ester may be mixed with other solvent. Further, depending upon the material for the negative electrode active material, there may be a case where the charge/discharge characteristics, cycle
20 durability or charge/discharge efficiency can be improved by a combined use of a chain carbonic ester and a cyclic carbonic ester.

 Further, to such an organic solvent, a vinylidene fluoride/hexafluoropropylene copolymer (for example,
25 Keiner, tradename, manufactured by Atochem Company) and vinylidene fluoride/perfluoropropyl vinyl ether copolymer disclosed in JP-A-10-294131, may be added, and the

following solute may be added to obtain a gel polymer electrolyte.

As the solute, it is preferred to use at least one member of lithium salts containing e.g. ClO_4^- , CF_3SO_3^- , BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , CF_3CO_2^- or $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ as an anion. For the above electrolyte solution or polymer electrolyte, it is preferred to add the electrolyte made of a lithium salt to the above solvent or solvent-containing polymer at a concentration of from 0.2 to 2.0 mol/l. If the concentration departs from this range, the ion conductivity tends to decrease, and the electrical conductivity of the electrolyte tends to decrease. The concentration is more preferably adjusted to be from 0.5 to 1.5 mol/l.

In the lithium cell employing a positive electrode active material of the present invention, as the negative electrode active material, a material capable of absorbing and desorbing lithium ions, is employed. The material for such a negative electrode active material is not particularly limited, but, it may, for example, be a lithium metal, a lithium alloy, a carbon material, an oxide composed mainly of a metal of Group 14 or 15 of the Periodic Table, a carbon compound, a silicon carbide compound, a silicon oxide compound, titanium sulfide or a boron carbide compound. As the carbon material, one obtained by thermally decomposing an organic material by various thermal decomposition conditions, or artificial

graphite, natural graphite, soil graphite, expanded graphite or scaly graphite, may, for example, be used.

Further, as the oxide, a compound composed mainly of tin oxide, may be used. As the negative electrode current collector, a copper foil or a nickel foil may, for example, be used.

The negative electrode and the positive electrode employing the positive electrode active material of the present invention is obtained preferably by kneading the active material with an organic solvent to obtain a slurry, and coating the slurry on a metal foil current collector, followed by drying and pressing. There is no particular restriction as to the shape of the lithium cell of the present invention. A sheet shape (so-called film shape), folded-shape, wounded bottomed cylindrical shape or a button shape, may suitably be selected depending upon the particular application.

【Examples】

Now, the present invention will be described in further detail with reference to Examples, but it should be understood that the present invention is by no means restricted to such Examples.

EXAMPLE 1

A cobalt oxyhydroxide powder having an average particle size of 10 μm and a specific surface area of 66 m^2/g , a lithium carbonate powder having an average particle size of 15 μm and a specific surface area of 1.2

m²/g and a zirconium oxide (ZrO₂) powder having an average particle size of 8.1 μm and a specific surface area of 15 m²/g, were mixed. The mixing ratio was such that the composition would be LiCo_{0.998}Zr_{0.002}O₂ after firing. These three types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the positive electrode active material powder), the X-ray diffraction spectrum was obtained by using RINT 2100 model X-ray diffraction apparatus, manufactured by Rigaku Corporation. By this powder X-ray diffraction using CuK_α ray, the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was 0.117° .

The LiCo_{0.998}Zr_{0.002}O₂ powder thus obtained, acetylene black and a polytetrafluoroethylene powder, were mixed in a weight ratio of 80/16/4 and kneaded while adding toluene, followed by drying to obtain a positive electrode plate having a thickness of 150 μm.

And, two stainless steel simple closed cells were assembled in an argon glove box, by using an aluminum foil having a thickness of 20 μm as a positive electrode current collector, using a porous polypropylene film having a thickness of 25 μm as a separator, using a metal lithium foil having a thickness of 500 μm as a negative electrode, using a nickel foil of 20 μm as a negative

electrode current collector, and using 1M LiPF₆/EC+DEC (1:1) as an electrolyte.

With respect to these two cells, firstly, charging was carried out to 4.3 V at a load current of 75 mA per g of the positive electrode active material at 25°C, and discharging was carried out to 2.5 V at an applied current of 75 mA per g of the positive electrode active material, whereby the initial discharge capacity was obtained. With respect to one cell, the charge/discharge cycle test was further carried out 40 times. Further, the other cell was charged at 25°C and then cooled to -10°C. Then, discharging was carried out to 2.5 V by a load current of 75 mA per g of the positive electrode active material, whereby the initial discharge capacity at -10°C was obtained, and the capacity development rate at -10°C was obtained, on the basis that the initial electric capacity at 25°C was 100%.

The initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 95.8%. Further, the capacity developing rate at -10°C was 68%.

EXAMPLE 2

A cobalt oxyhydroxide powder having an average particle size of 10 μm and a specific surface area of 66 m²/g, a lithium carbonate powder having an average particle size of 15 μm and a specific surface area of 1.2 m²/g and a hafnium oxide (HfO₂) powder having an average

particle size of 0.4 μm and a specific surface area of 7.2 m^2/g , were mixed. The mixing ratio was such that the composition would be $\text{LiCo}_{0.998}\text{Hf}_{0.002}\text{O}_2$ after firing. These three types of powders were dry-blended and then fired at
5 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the positive electrode active material powder), the X-ray
10 diffraction spectrum was obtained by using RINT 2100 model X-ray diffraction apparatus, manufactured by Rigaku Corporation. By this powder X-ray diffraction using CuK_α ray, the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was 0.119° .

15 The $\text{LiCo}_{0.998}\text{Hf}_{0.002}\text{O}_2$ powder thus obtained, acetylene black and a polytetrafluoroethylene powder, were mixed in a weight ratio of 80/16/4 and kneaded while adding toluene, followed by drying to obtain a positive electrode plate having a thickness of 150 μm .

20 And, two stainless steel simple closed cells were assembled in an argon glove box, by using an aluminum foil having a thickness of 20 μm as a positive electrode current collector, using a porous polypropylene film having a thickness of 25 μm as a separator, using a metal
25 lithium foil having a thickness of 500 μm as a negative electrode, using a nickel foil of 20 μm as a negative electrode current collector, and using 1M $\text{LiPF}_6/\text{EC}+\text{DEC}$

(1:1) as an electrolyte.

With respect to these two cells, firstly, charging was carried out to 4.3 V at a load current of 75 mA per g of the positive electrode active material at 25°C, and
5 discharging was carried out to 2.5 V at an applied current of 75 mA per g of the positive electrode active material, whereby the initial discharge capacity was obtained. With respect to one cell, the charge/discharge cycle test was further carried out 40 times. Further,
10 the other cell was charged at 25°C and then cooled to -10°C. Then, discharging was carried out to 2.5 V by a load current of 75 mA per g of the positive electrode active material, whereby the initial discharge capacity at -10°C was obtained, and the capacity development rate
15 at -10°C was obtained, on the basis that the initial electric capacity at 25°C was 100%.

The initial discharge capacity at from 2.5 to 4.3 V at 25°C was 149 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 96.0%. Further, the
20 capacity developing rate at -10°C was 70%.

EXAMPLE 3

A cobalt oxyhydroxide powder having an average particle size of 8 μm and a specific surface area of 40 m^2/g , a lithium carbonate powder having an average
25 particle size of 22 μm and a specific surface area of 0.64 m^2/g and a zirconium oxide (ZrO_2) powder having an average particle size of 8.1 μm and a specific surface

area of 16 m²/g, were mixed. The mixing ratio was such that the composition would be LiCo_{0.994}Zr_{0.006}O₂ after firing. These three types of powders were dry-blended and then fired at 890°C for 15 hours in an atmosphere
5 having the oxygen concentration adjusted to 19 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the positive electrode active material powder), the X-ray diffraction spectrum was obtained by using RINT 2100
10 model X-ray diffraction apparatus, manufactured by Rigaku Corporation. By this powder X-ray diffraction using CuK_α ray, the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was 0.128° .

The LiCo_{0.994}Zr_{0.006}O₂ powder thus obtained, acetylene
15 black and a polytetrafluoroethylene powder, were mixed in a weight ratio of 80/16/4 and kneaded while adding toluene, followed by drying to obtain a positive electrode plate having a thickness of 150 μm.

And, two stainless steel simple closed cells were
20 assembled in an argon glove box, by using an aluminum foil having a thickness of 20 μm as a positive electrode current collector, using a porous polypropylene film having a thickness of 25 μm as a separator, using a metal lithium foil having a thickness of 500 μm as a negative
25 electrode, using a nickel foil of 20 μm as a negative electrode current collector, and using 1M LiPF₆/EC+DEC (1:1) as an electrolyte.

With respect to these two cells, firstly, charging was carried out to 4.3 V at a load current of 75 mA per g of the positive electrode active material at 25°C, and discharging was carried out to 2.5 V at an applied
5 current of 75 mA per g of the positive electrode active material, whereby the initial discharge capacity was obtained. With respect to one cell, the charge/discharge cycle test was further carried out 40 times. Further, the other cell was charged at 25°C and then cooled to -
10 10°C. Then, discharging was carried out to 2.5 V by a load current of 75 mA per g of the positive electrode active material, whereby the initial discharge capacity at -10°C was obtained, and the capacity development rate at -10°C was obtained, on the basis that the initial
15 electric capacity at 25°C was 100%.

The initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 95.7%. Further, the capacity developing rate at -10°C was 72%.

20 COMPARATIVE EXAMPLE 1

A positive electrode active material was synthesized in the same manner as in Example 1 except that no zirconium oxide was added. The half-width of the diffraction peak for (110) face measured in the same
25 manner as in Example 1, was 0.098°. Further, the measurement of cell performance was carried out in the same manner as in Example 1, whereby the initial

discharge capacity at 25°C was 149 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 94.8%. Further, the capacity developing rate at -10°C was 54%.

5 COMPARATIVE EXAMPLE 2

A positive electrode active material was synthesized in the same manner as in Example 1 except that the added amount of zirconium oxide was changed and the mixing ratio was such that the composition would be
10 $\text{LiCo}_{0.95}\text{Zr}_{0.05}\text{O}_2$ after firing. The half-width of the diffraction peak for (110) face measured in the same manner as in Example 1, was 0.183°. Further, the measurement of cell performance was carried out in the same manner as in Example 1, whereby the initial
15 discharge capacity at 25°C was 140 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 93.8%. Further, the capacity developing rate at -10°C was 68%.

【Effects of the Invention】

20 As described above, according to the present invention, a positive electrode active material for a lithium secondary cell which has a large electric capacity, good low temperature discharge characteristics, excellent charge/discharge cycle durability and high
25 safety, will be provided.

【TYPE OF DOCUMENT】 ABSTRACT

【SUMMARY】

【OBJECT】

A composite oxide suitable for a non-aqueous
5 electrolytic secondary cell which can be used in a wide
range of voltage, has a large electric capacity and
excellent low temperature performance and is excellent in
the durability for charge-discharge cycles, is presented.

【MEANS OF ACCOMPLISHING THE OBJECT】

10 The composite oxide is a hexagonal lithium-cobalt
composite oxide for a lithium secondary cell, which is
represented by the formula $\text{LiCo}_{1-x}\text{M}_x\text{O}_2$, (wherein $0.0005 \leq x \leq$
0.02 and M is at least one member selected from the group
consisting of Zr and Hf), and which has a half-width of
15 the diffraction peak for (110) face at $2\theta = 66.5 \pm 1^\circ$, of
from 0.080 to 0.180° , as measured by the X-ray
diffraction using CuK_α as a ray source.

【SELECTED FIGURE】 No Selected Figure